

**CHARACTERIZATION OF SOLUBLE MACROMOLECULAR  
OXIDATIVELY REACTIVE SPECIES (SMORS)  
FROM MIDDLE DISTILLATE DIESEL  
FUELS: THEIR ORIGIN AND ROLE IN INSTABILITY**

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**INTRODUCTION** In diesel fuels which are oxidatively unstable and at least 6 months old, it has been shown that a solid phase can be isolated from the filtered fuels by methanol extraction followed by precipitation with hexane. The weight of this material is directly proportional to the amount of sludge which forms by both accelerated storage stability tests and by continued field aging of the fuels. We have suggested that the presence of this extraction induced precipitate (EIP) or fuel Soluble, Macromolecular, Oxidatively Reactive Species (SMORS) in these fuels thus accounts for the production of thermally induced precipitate (TIP) or insoluble sediment during oxidative aging of diesel fuels.<sup>1,2,3</sup> In this paper the acronym EIP will be used in place of SMORS in most cases.

This paper describes and summarizes the characterization studies performed to date on the EIP from representative fuels which are all greater than 6 months past production. The origin and apparent role of SMORS in sediment formation in diesel fuels is discussed.

**EXPERIMENTAL** All procedures for filtering fuels, and for extraction and precipitation steps used in isolating the EIP from fuels have been described in detail elsewhere.<sup>1,2</sup>

GC analysis was performed on samples dissolved in methanol using a Hewlett-Packard Model 5890 GC equipped with flame ionization detector and HP Model 3392 integrator. A 50-m methylated silicone (nonpolar) capillary column was used for separation. Experimental conditions included an inlet temperature of 280 °C, a split ratio of 22:1 and a column temperature program between 100 °C and 280 °C. A 1-min initial hold at 100 °C was used; the temperature was then ramped at 5 °C/min to 280 °C and then held at that temperature for 10 minutes.

The field ionization mass spectral (FIMS) system used for this work has been described elsewhere.<sup>4,5</sup> At the end of each run, the sample holder is retrieved and weighed to determine the fraction that was volatilized during the pyrolysis.

Low voltage electron impact, high resolution mass spectrometry was used to determine the exact masses of several of the key fragment ions, when the EIP was introduced by pyrolysis (identical to the FIMS sample introduction).

Elemental analyses and molecular weight determinations by vapor pressure osmometry were provided by commercial laboratories. All elements including oxygen (but not sulfur) were determined by combustion and not by difference.

All blended stocks used were prepared in the laboratory as 80/20 straight run/LCO mixtures (v/v). Blends were always filtered before extraction. The straight run fuel used was a water-white, clear stock obtained from the same refinery that furnished LCO-3. All fuels and blends are described in earlier papers in this series<sup>1,2,3</sup> and a consistent fuel code has been continued.

**RESULTS AND DISCUSSION** Elemental Analyses/Molecular Weights by Vapor Pressure Osmometry. Table 1 summarizes the elemental analysis data (CHON) obtained for solids (EIP) extracted from 3 light cycle oils (LCOs) and 5 blends. Data are as received and not normalized to 100%. The elemental analysis results for 20% LCO/80% SR EIP from blends is shown in the bottom half of Table 1. Here it is interesting to compare the blends to the LCO's. In general the EIP from blends have somewhat higher oxygen and lower carbon content indicating that EIP from blends is more polar than from LCO's. If higher polarity equates to higher chemical reactivity, then this finding supports the long-known fact that blending reactive LCO's with non-reactive SR streams does not usually dilute the sludge forming tendencies in a direct ratio. With very reactive LCO's, dilution by as much as 70%

SR sometimes has no effect on reducing sludge formation amounts in the resulting blends.<sup>6</sup> It is noteworthy that these blends are made up immediately before the EIP is isolated for elemental analysis and thus the chemical changes in elemental analysis are due to the blending process itself and not any subsequent aging of LCO EIP in the resulting blend.

Table 2 presents a summary of the blend data from Table 1 for EIP which is normalized to 100% in order to determine an empirical formula. Data for typical average elemental analyses of TIP or sediment is given also.<sup>7</sup> The trend for blend EIP to contain more oxygen is continued in the TIP and this is reflected in the average empirical formula which contains an additional  $\text{CH}_2 + \text{H}_2\text{O}$  compared with typical EIP.

Included in Table 3 are molecular weight data obtained by vapor pressure osmometry. Note that these data are quite consistent with the molecular weight data obtained by size-exclusion chromatography (570 vs 600-900) considering errors inherent in, in particular single point VPO determinations and in size-exclusion data for molecular weights <1000 Da. for molecular shapes which are likely to be quite different from those of the standards used.

**Gas Chromatography.** When EIP samples are isolated from the methanol extract and then re-dissolved in methanol they may be subjected to analysis by GC. The dissolved EIP gave surprisingly simple chromatograms with no major peaks that would correspond with any of the moieties commonly thought to be precursors to instability. This led to the conclusion that the methanol fraction contained the presence of higher molecular weight species which were not eluted under the standard experimental GC conditions employed. This also demonstrates very clearly that the EIP does not contain any entrapped fuel species. This is an important fact in the subsequent interpretation of the PYR/FIMS data.

**Pyrolysis/Field Ionization Mass Spectrometry (PYR/FIMS).** Two representative EIP samples were chosen for PYR/FIMS analysis. These were LCO-3 and LCO-5. The EIP were isolated as a solid powder and then completely dissolved in toluene in order to introduce a homogeneous sample into the glass capillary for pyrolysis field ionization MS. Most of the toluene was removed by evaporation and then the remaining solid sample of EIP was heated at a controlled rate up to 500° C in the high vacuum source region of the MS. Subsequent weighing of the capillary tube revealed that essentially 100% by weight of the EIP had been pyrolyzed and volatilized by this procedure. Identical analyses of TIP/sludge generally show that less than 60% of the sample is consumed after pyrolysis leaving considerable char in the sample tube.

Representative data for LCO-3 are shown in Table 4. Residual toluene solvent is not shown in the figure but volatilized between approximately 30 and 125° C. Since no other ions up to 300 daltons were seen in this region it can be concluded that the original EIP samples were essentially free of entrapped fuel. In addition, as noted above, GC analysis of EIP which are re-dissolved in methanol reveal no entrapped fuel components.

The total ion mass chromatograms for the pyrolysis FIMS are quite complex. This underscores the tremendous amount of pyrolysis that the EIP samples are undergoing. At the same time it is noteworthy that the entire sample is volatilized/pyrolyzed in a fairly narrow range from 175 to 375° C. The calculated number average molecular weight of the LCO-5 EIP by this process is 582 daltons and the calculated weight average molecular weight is 687. This is in fairly good agreement for the VPO determined molecular weight of this sample (see Table 3).

Due to the complexity of presenting the data in the form of mass pyrograms for subsequent interpretation, an alternative approach has been taken. About half of the total ion current of the mass pyrogram is contained in a number of series of homologous ions separated by 14 dalton increments. These homologous ion series have been arbitrarily assigned a mass identification number, usually one of the lowest mass ions in a particular series. In the case of data for Table 4 only the most intense ion in a particular series was used to generate the temperature profile. In the case of data for Table 5 the sum of all the ions in a particularly identified ion series was determined. The mass intensity values in all cases have been taken from normalized spectra. In addition, the base peaks for all three spectra (in ion counts) were very close in intensity. For this reason the ion counts were not converted to percent relative abundance as is normally done but instead are converted to a normalized ion count. At this point it is possible to attempt a more detailed analysis of the nature of the EIP sample as revealed by the mass pyrogram in Table 4. The 9 ion series identified account

for the 9 most intense sets of masses. Most of the mass peaks in Table 4 are pyrolysis fragments of the high molecular weight EIP. This is supported by the fact that the major series below 300 daltons continue to form over the entire temperature range between 90 and 360° C. As the temperature of the pyrolysis increases the pyrolyzate fragments of higher molecular weight begin to appear (between 300 and 600 daltons) up to temperatures of 400° C.

As conjectured in an earlier paper in this series<sup>1</sup>, one of the two possible alternative origins of EIP is that a fuel soluble macromolecular species (possibly porphyrinic in nature) is carried over into the fluid catalytic cracker by the feed stock and ends up in the product blending stream. This macromolecular species could then further oxidize (making it more polar and soluble in methanol, at which point it is EIP). Finally further oxidation and condensation reactions with reactive fuel monomers precipitates the final product insoluble sediment or sludge.

Since the above conjecture rests upon a geochemical/processing origin one would then expect that the EIP from various sources would be somewhat similar at least in gross structural features. The PYR/FIMS data for the two LCOs given in Table 5 strongly indicates that this alternative origin for EIP is probably not correct. Although there are some strong similarities in the three EIP samples such as the mass series at 131 and 309, there exist major dissimilarities. In addition to this, a common geochemical origin for EIP would be porphyrinic in nature and the PYR/FIMS fragments of such an EIP moiety would result in significant amounts of pyrrolic species evolved below 300 daltons and these do not occur.

The traditional explanation for the origin of TIP/sludge or sediment postulates reactive monomeric fuel components which oxidize and condense to form larger and more polar and less fuel soluble species. The fact that the EIP species must themselves further oxidize and condense to form TIP/sludge means that we now have a probe of some intermediate stage in sludge formation from reactive fuel monomers which is itself a simpler species compositionally and is much more amenable to analysis. In fact, the EIP themselves are simply produced by reactive fuel monomeric species. This last statement suggests that the detailed chemical nature of the EIP and the sediment itself must be quite fuel dependent and the data in Table 5 support this very clearly.

This information together with the fact that the PYR/FIMS data clearly support the elemental analysis data of the EIP which implicates nitrogen and oxygen containing compounds underscores the need to continue to determine the precursors of EIP in the original fuel. The fact that EIP are formed from reactive fuel monomers implies that freshly refined LCO's will not initially have EIP present and this is the subject of our current investigations. If an LCO or LCO blend has formed as little as 20 mg/L of EIP, then the LCO itself is probably of little use in studies designed to determine the compositional precursors of either EIP or TIP/sludge. It is for this reason that many very carefully performed studies to date have not been able to pinpoint the real precursors of sludge formation. Certainly if an LCO contains high total nitrogen or indoles content it also contains the real precursors to sludge. These indicators, however, are not able to be directly or quantitatively linked to any given fuel's sludge forming tendency.

**CONCLUSIONS** All of the EIP samples analyzed for this work were from fuels which had already developed EIP, i.e., they were at least 6 months old since production. Molecular weights from VPO and PYR/FIMS were all consistent in the range of 650 to 1000 daltons. The EIP have proven to be considerably easier to analyze than the actual sludge which they apparently produce ultimately.

Since it has been shown that the EIP do not arise as a geochemical/processing artifact it can be concluded that they arise from the oxidation and condensation of reactive fuel monomers. Clues as to the nature of these fuel species are found in the elemental analysis and empirical formulas for EIP which indicates much involvement of oxygen and nitrogen. Further information from the high resolution mass spectral empirical formulas and from the PYR/FIMS indicates that nitrogen containing precursors in the fuel with a formula of  $C_nH_{2n-9}N$  and  $C_nH_{2n-15}$  are involved in the generation of EIP. The 2n-9 class includes such isoelectronic possibilities as indoles, divinyl pyridines and dihydroquinolines. The 2n-15 class includes such isoelectronic possibilities as benzoindoles, phenalidines, divinyl quinolines and carbazoles.

The EIP are more amenable to PYR/FIMS analysis as evidenced by their complete pyrolysis than the more highly oxidized and polar TIP/sludge. Even so, the PYR/FIMS technique subjects the EIP to a tremendous amount of pyrolysis. Because of this the interpretation of pyrolyzate ions to reconstruct the formation of EIP is not possible.

Only freshly refined, unhydrotreated, catalytically cracked LCO material will be suitable for future studies involving the determination of the fuel precursors of EIP and whether the formation of EIP can be inhibited by antioxidant additives. Essentially no work on the determination of fuel precursors to sludge to date has appreciated the importance of this fact. Certainly no work presented to date has verified the initial absence of EIP before beginning a detailed compositional analysis and this is essential. By the time a measurable amount of EIP has formed, it is quite possible that all of the actual precursors to sludge are already well on their way to the dimer/trimer stage and hence no longer amenable to simple GC analysis techniques to monitor their depletion from the fuel.

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Table 1. Elemental Analysis of Selected EIP. Direct determination of CHON.

Fuel Code	Fuel Type	% C	% H	% O	% N	% Total
LCO-2	100% LCO	79.4	6.1	9.9	2.5	97.9
LCO-3	100% LCO	83.2	6.5	4.6	4.8	99.1
LCO-5	100% LCO	84.2	6.7	3.1	5.6	99.6
B-2	20% LCO	75.3	6.1	10.1	4.9	96.4
B-5	20% LCO	79.4	6.3	7.5	3.0	96.2
B-5*	20% LCO	75.2	6.4	9.8	5.5	96.9
B-13	20% LCO	76.5	6.4	9.1	4.9	96.9
B-14	20% LCO	76.5	5.8	10.4	3.3	96.0

\*EIP determined after ASTM D5304 stress test.

Fuel Code is: LCO = catalytically cracked light cycle oil

B = blend of 20% LCO + 80% SR v/v

Table 2. Elemental Analysis Averages (normalized to 100%) for a wide range of 20% LCO blends for EIP and Sediment. Empirical formula also computed from these data.

Property	EIP	Sediment/TIP
% Carbon	79.4	75.4
% Hydrogen	6.4	6.9
% Oxygen	9.7	13.7
% Nitrogen	4.5	4.0
Empirical Formula	$C_{21}H_{20}O_2N$	$C_{22}H_{24}O_3N$

Table 3. Molecular Weight Analysis by Vapor Pressure Osmometry (VPO) for selected EIP samples (in Daltons).

Fuel Code	Single Point	Triple Point
LCO-3	513	525
LCO-5	486	679

Table 4. EIP of LCO-3 analyzed by pyrolysis FIMS. Mass ID referred to the major mass in that homologous mass series from the pyrolyzate. As the temperature of the sample is raised from 100 to 400 C the major ion intensities (raw data counts) are summed for that temperature range. (-) indicates a value close to zero ion counts.

Mass ID	Probe/Sample Temperature Range °C						SUM
	90-150	164-201	203-250	254-299	303-355	359-399	
131	1.2	2.8	4.5	2.2	0.6	0.1	11.4
180	4.0	6.5	1.0	-	-	-	11.5
181	1.5	1.1	1.0	0.6	0.3	-	4.5
202	0.7	1.2	0.3	-	-	-	2.2
309	0.3	0.9	3.7	1.5	0.4	-	6.8
438	-	0.4	5.2	6.1	1.5	0.1	13.3
563	-	-	0.7	9.7	12.5	2.1	25.0
580	-	-	3.5	4.2	0.5	0.5	8.9
581	-	-	2.2	3.4	1.0	0.7	7.3
SUM-->	7.7	12.9	22.1	27.7	16.8	3.5	90.9

Table 5. Pyrolysis FIMS comparative analysis of several EIP solids. The major homologous series are identified by a mass which is generally the highest in the series, but not always. Compare these values for the sum of the homologous series for the entire pyrolysis temperature range to the totals for an individual mass given in Table 4. Compound type empirical formulas for the ion series given is from independent high resolution exact mass (to 10<sup>-4</sup> mass units) data.

Mass Series ID	Empirical Formula	LCO-3	LCO-5
131	C <sub>9</sub> H <sub>9</sub> N	34	21
156	---	0	20
180	C <sub>13</sub> H <sub>10</sub> N	28	51
181	C <sub>13</sub> H <sub>11</sub> N	14	57
202	---	5	24
261	---	0	0
309	C <sub>22</sub> H <sub>15</sub> NO	19	35
438	C <sub>31</sub> H <sub>22</sub> N <sub>2</sub> O	41	54
563	---	78	9
580	---	25	0
581	---	23	0